# Letters to the Editor

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## ON THE POTENTIAL ENERGY CURVES OF DIATOMIC COPPER HALIDES

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The spectra emitted by copper halides are characterized by the appearance of a large number of systems in the visible region of the spectrum. The rotational constants for these molecules in their various electronic states have become known recently and we now report the experimental or "true" potential energy curves for these electronic states. This study was prompted to some extent by the previous work on silver hydride and silver halides (Singh *et al*, 1965) where the true potential curves for the excited states were found to have shapes in accordance with the explanation suggested by Learner (1962) for the observed perturbations. Moreover it has been found in a large number of cases that presence of ionic character in the binding makes the use of empirical potential curves unreliable. It is expected that these molecules will have decreasing ionic contribution to their binding as we go from CuF to CuI and this provided a good opportunity to test the validity of the above statement.

The method used for the construction of the true potential energy curves is the well known RKRV method which enables one to calculate the classical turning points for each vibrational level. The data needed for the calculation were obtained from Ritschl (1927) and Woods (1943) for CuF, from Rao, Brody and Asundi (1962) for CuCl and from Nair (1967) for CuI. As expected from the known $T_e$ values the curves for B and C states of CuCl are very close to each other as are those for D and E states of the same molecule and the two curves

cross at certain points (fig. 1). There has been no observation of any perturbation though some are bound to occur. Of course there is an anomalous Λ

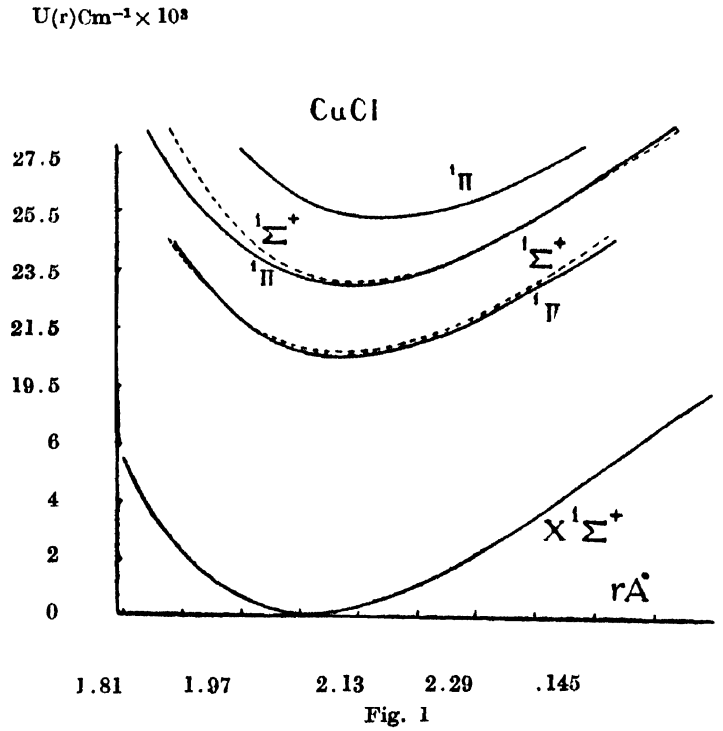


Fig. 1

doubling in the two $^1\Pi$ states due to the effect of the two close $^1\Sigma$ states. The potential energy curves of CuF and CuI are also drawn. As the rotational

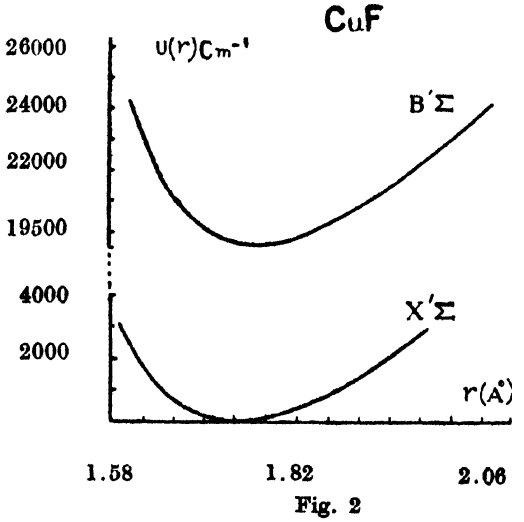


Fig. 2

constants for only a few states are known in the case of these molecules the potential curves of only two states for each are drawn. The curves are normal and show no anomaly. One of these (for CuI) is shown in fig 2.

The dissociation energies of molecular electronic states can often be estimated by using an empirical potential function to approximate the true potential energy curves (Steele 1964, Singh *et al* 1965). The three parameter Lippincott function has been found suitable in a number of cases. In case of molecular states having appreciable ionic character, however, this method of curve fitting leads to very low values of the dissociation energies (Thakur *et al*, 1967). For CuF the Birge-Sponer extrapolation leads to a value of 3 ev while the curve fitting method leads to only 1.5 ev In case of CuCl the linear Birge-Sponer extrapolation leads to 3.3 ev while thermochemical method yields a value 3.80 ev The

RKRV curve for CuI

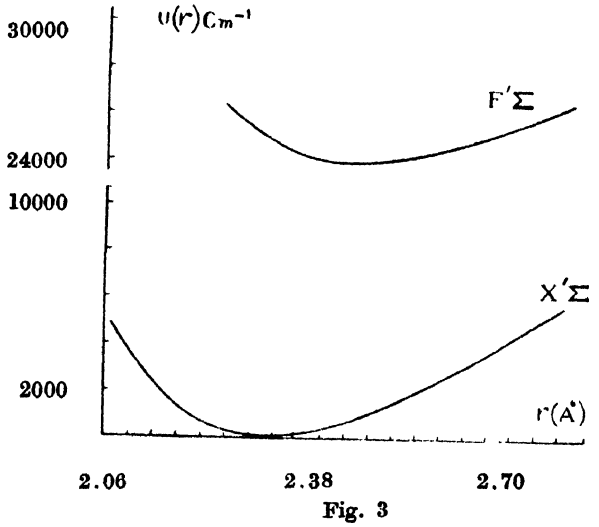


Fig. 3

curve fitting using Lippincott function yields a value 2.4 ev It is expected from the low electron affinity of iodine in comparison to F and Cl that in CuI the ionic structures will appreciably affect only the bindings of the highly excited states and the ground state be reasonably free from ionic effects. The most reliable value of De(CuI) according to Gaydon (1947) is 2 ev obtained from thermochemica data and we obtain a value of 2.05 ev in very good agreement with this va ue.

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# BREAKDOWN IN THERMAL PLASMAS

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The phenomenon of breakdown or transition in gas discharges, such as from dark discharge to glow or from glow to arc, has been studied by many workers (Meek and Craggs, 1953, Gambling and Edels, 1956, von Engel, 1965) under low and high pressures and temperatures. Recently, due to the engineering developments in the use of high temperature and pressure plasmas for direct energy conversion projects, considerable interest in the study of thermal plasmas is growing amongst scientists and engineers (Kerrebrock, 1963, Ralph, 1963, George 1963, Sakuntala, 1964 and 1965). The present letter deals with a correction relating to the theory given by Sakuntala (1965).

In thermal plasmas described by Sakuntala (1965), the breakdown potentials are considerably lower than the expected values by the general theory. In a gas at relatively high temperature, the plasma is due to thermal ionisation in the hot seed vapour, thermionic emission from the hot electrode surfaces and electron-atom collisions in the gas between the electrodes. Considering these three factors, the space charge limited current at any point $x$ between the electrodes, distant $D$, can be derived from Poisson's equation,

$$\frac{d^2V}{dx^2} = \frac{-dX}{dx} = 4\pi \left\{ \frac{j^- e^{ax}}{\mu^- X} - \frac{j^-(e^{aD} - e^{ax})}{\mu^+ X} \right\} e.s.u \qquad (1)$$